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IN-PLACE POLYMERIZATIONS OF ELECTROPHILIC OLEFINS.(U)
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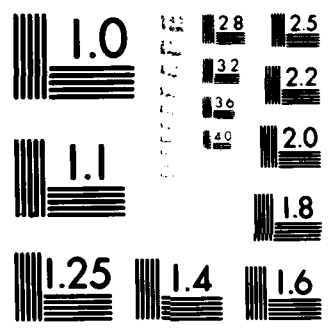
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Electrophilic olefins, new monomers, multi-substituted monomers, quino-dimethanes, xylenes, methylenecyclobutanes, electrophilic butadiens, ion-radical propagation, Organic Periodic Table.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A. Introduction

B (1) ^{Alpha} α -Carbomethoxymaleic anhydride, a highly reactive new monomer was synthesized. It oligomerized, copolymerized and cycloadded to electro-rich monomers.

C (2) Dimethyl and diethyl dicyanofumarate, tetrasubstituted olefins, copolymerize with p-methoxystyrene.

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20. ABSTRACT CONTINUED

- D. New 7,7,8,8-tetrasubstituted quinodimethanes containing cyano and ester groups were synthesized and isolated. They homo- and copolymerized and formed charge transfer complexes with tetrathiofulvalene.
- E. 3-Methylenecyclobutene-1-carbonitrile, a new monomer was synthesized and polymerized.
- F. 1,3-Dicyano and 1,3-dicarbomethoxybutadienes, highly reactive new monomers, were synthesized. They were exceptionally reactive new monomers.
- G. NMR study of poly-bicyclobutane-1-carbonitrile was done.
- H. Three new theories, involving cation-radical or anion-radical propagation and an Organic Chemist's Periodic Table, were proposed.

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DAAG29-77-G0231
FINAL CUMULATIVE REPORT TO
U. S. ARMY RESEARCH OFFICE

by
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In-Place Polymerizations of Electrophilic Olefins

A. Introduction

The search for new plastics and materials continues as scientific and industrial requirements continue to become more demanding. A particularly important group of such materials are those formed in place, i.e., by addition polymerization. Here, no small molecules are split out as in polycondensation, and shaped objects can be obtained directly from monomers. Such polymerizations can be either of the vinyl or ring opening types. However, currently available monomers, which polymerize by either of these methods have been extensively studied already, and so the search for new monomers becomes increasingly important.

Demand by technology for materials retaining good properties under extreme conditions continues to grow. While conventional commercial polymers meet these requirements to some extent, the search for novel polymers and copolymers continues to be appropriate.

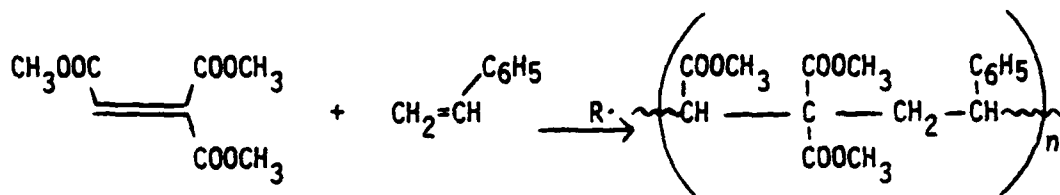
Inasmuch as industry is doing less work of this kind, it becomes more urgent for University researchers to fill this need.

Our work has emphasized electrophilic monomers, containing especially cyano and carbomethoxy groups. Such groups often confer stability and good mechanical properties to polymers.

B. Planar Electrophilic Trisubstituted Ethylenes

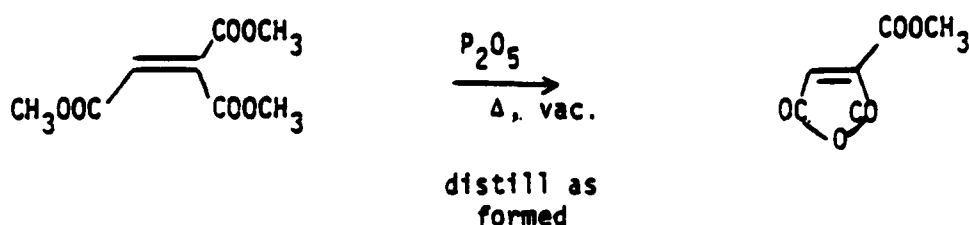
1. Earlier Work

Trisubstituted ethylenes had been a neglected class of monomers. In the past (with U. S. Army support) we have made numerous such monomers such as tricyanoethylene and tricarbomethoxyethylene. Although they did not homopolymerize, they were highly reactive as comonomers with nucleophilic monosubstituted ethylenes. A wide variety of alternating 1:1 copolymers was obtained by free radical initiation.

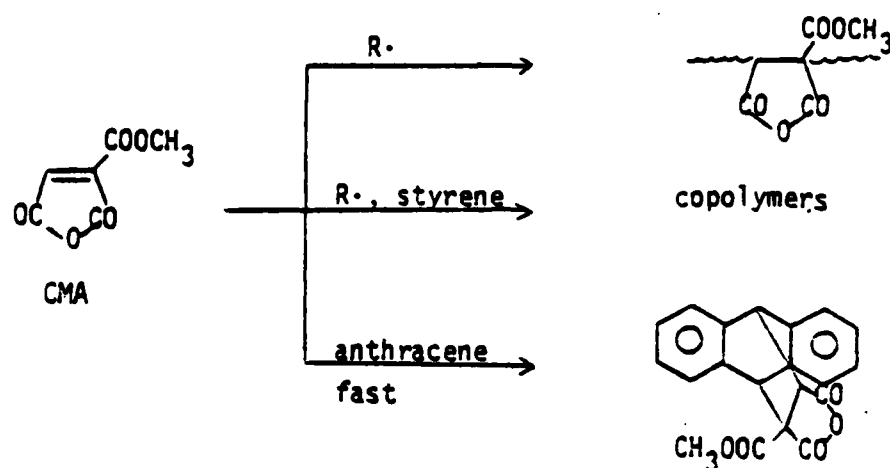


2. Recent Results

We have emphasized a special group of such monomers. These are the cases wherein the substituents are part of a ring, as in maleic anhydride or maleimide. These monomers should show enhanced reactivity in that the flat ring reduces steric hindrance at the β position and secondly, holds the carbonyl groups flat to permit effective overlap of the odd electron or anion at all times. An electrophilic trisubstituted ring-containing ethylene should be still more reactive. Remarkably, we were unable to find a single example of such a molecule in the literature. We attempted the synthesis of such compounds by standard procedures for two years without success. However, more recently, we obtained α -carbomethoxy-maleic anhydride through a novel synthesis from our earlier monomer tricarbomethoxyethylene:



Carbomethoxymaleic anhydride proved to be remarkably reactive. It homopolymerized, although only to rather low homopolymers.

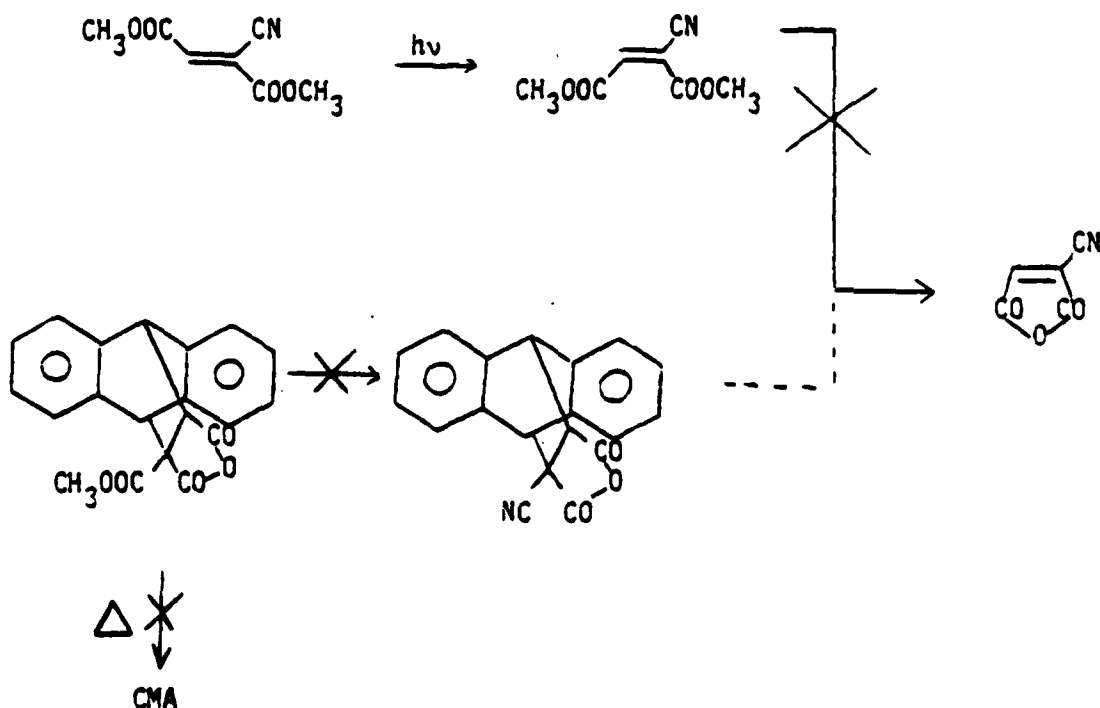


This is unique for a trisubstituted ethylene; even chloromaleic anhydride has not been reported to homopolymerize. Secondly, CMA copolymerized readily with a wide variety of vinyl monomers. These copolymerizations were remarkable in that in many cases no initiator was required. Attempts to establish whether these copolymerizations were radical or anionic in nature by adding inhibitors for these processes were not conclusive and more work is needed. Finally, CMA was highly reactive in 2+4 cycloadditions, even surpassing tetracyanoethylene in this regard.

In one respect, CMA did not prove to be reactive. We were unable to accomplish 2+2 cycloadditions to form cyclobutane derivatives, which we wanted as intermediate for our bicyclobutane monomers.

Thermal 2+2 cycloadditions of maleic anhydride itself also do not appear to occur.

In still more recent attempts to extend the scope of structures of this type, we have attempted to make cyanomaleic anhydride. However, this little molecule eluded our best efforts. We attempted to synthesize it by phosphoric anhydride cyclization of dimethylcyanomaleate. We were able to make the maleate by photochemical isomerization of the corresponding fumarate,⁵ but the cyclization did not succeed.



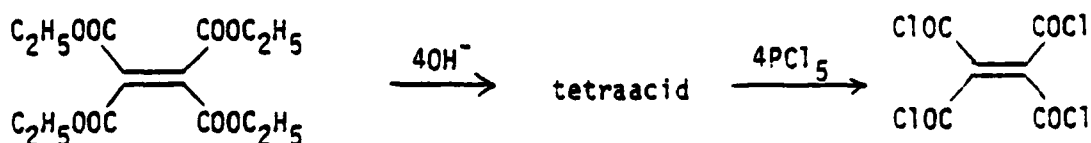
Secondly, although we have successfully carried out retro Diels-Alder reactions of various ethanoanthracenes, the thermolysis of the cycloadduct of CMA with anthracene failed. Probably, therefore, even had we been able to synthesize the anthracene-cyanomaleic anhydride, its thermolysis to generate the monomer would probably also have failed.

C. Electrophilic and Planar Tetrasubstituted Ethylenes

1. Earlier Work

No tetrasubstituted ethylenes have been confirmed to either homopolymerize or copolymerize except under extremely high pressures. Hopff had reported a few copolymers of tetrachloroethylene with ethylene, but aside from the ever-exceptional fluorocarbons, this is the only report so far.

An interesting molecule described in the literature was tetrachlorocarbonylene. This was reported by Polish workers

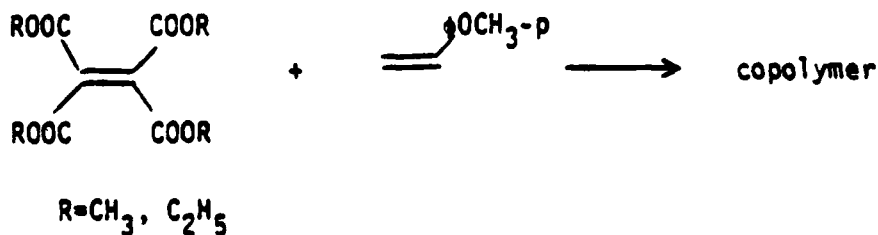


in the late 1930's, but no further work has been done. Dr. Daniel Bellus of Ciba-Geigy Company in Switzerland had suggested to us that such a compound might be even more electrophilic than tetracyanoethylene.

2. Recent Research

We duplicated the Polish preparation of tetrachlorocarbonylene. Its charge-transfer complexation constant (related to reactivity) has been determined, but is, regrettably, much smaller than tetracyanoethylene.

We found encouraging indications of copolymerization of tetracarbomethoxyethylene with p-methoxystyrene.

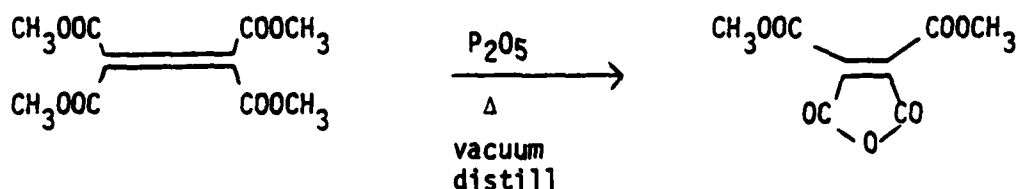


Encouraged by these preliminary results, we prepared dimethyl dicyanofumarate. It, and the corresponding ethyl ester, copolymerized



readily with electron-rich styrenes. These are the first copolymers of a tetrafunctional ethylene.

We extended our P_2O_5 cyclization synthesis to the corresponding dicarbomethoxymaleic anhydride:

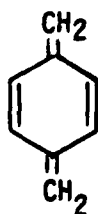


(Polish workers had made the diethyl ester previously) Insufficient time was unavailable for further study.

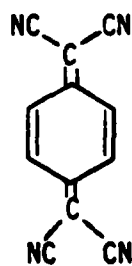
D. Electrophilic Quinodimethane

1. Earlier Work

p-Xylylene polymerizes so rapidly as to be unisolable; 7,7,8,8-tetracyanoquinodimethane (TCNQ) does not:



Polymer

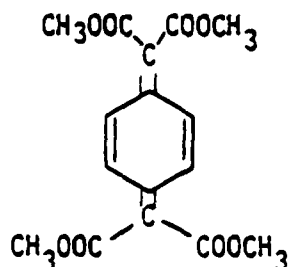


No Polymer

It appeared that other substituents might provide isolable, yet polymerizable monomers.

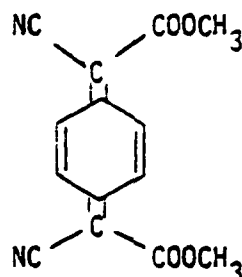
2. Recent Work

We improved a literature procedure and devised a good synthesis of 7,7,8,8-tetra (methoxycarbonyl) quinodimethane, TMQ:



It was isolable, yet underwent free radical-initiated homo- and copolymerization.

We have also synthesized:



A single pure isomer could be obtained. It polymerized readily and formed a black charge-transfer salt with TTF, tetrathiofulvalene.

E. Electrophilic 3-Methylenecyclobutene Derivatives

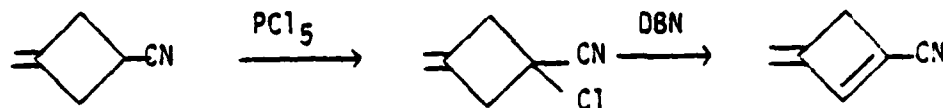
1. Earlier Work


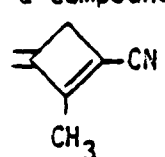
In the past, a few reports dealt with hydrocarbons containing the 3-methylenecyclobutene ring as monomers. They preferred to polymerize by 1,5-enchainment.

2. Recent Work

We prepared the first of a new group of this type, namely 3-methylenecyclobutene-1-carbonitrile. It was readily prepared from 3-methylenecyclobutanecarbonitrile by α -chlorination with phosphorous

pentachloride followed by dehydrochlorination. It was highly reactive in free radical polymerization.



Moreover, a compound earlier reported as  was shown to be . Its polymerization offered a second

cyclobutenecarbonitrile polymer.

F. Electrophilic 1,3-Dienes

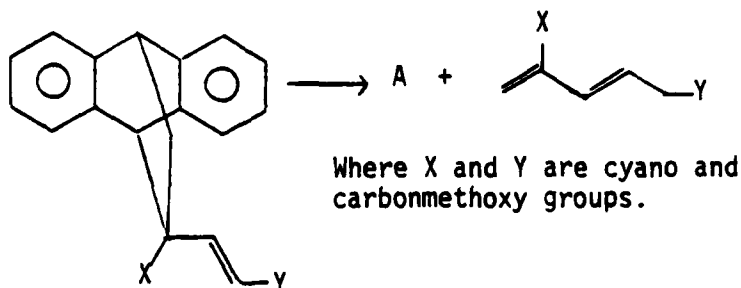
1. Earlier Work

In the past, very few electronegatively substituted 1,3-butadienes have been reported. The monosubstituted compounds have been studied to a reasonable extent, including 1- and 2- butadienes and the corresponding esters. However, among the disubstituted compounds, not much has been reported. The 1,4-derivatives do not appear to be very useful monomers. Recently, 2,3-dicyanobutadiene and its derivatives were prepared by R. L. Cobb of Phillips Petroleum Company. It was an interesting monomer in polymerizations and cycloadditions.

2. Recent Work

Yacoubi and Regelman tried unsuccessfully to make 1,3-dicyanobutadiene and the corresponding diester via acrylonitrile or methyl acrylate dimerization.


Ahn successfully prepared the four 1,3-, di (electronegatively substituted) butadienes as shown:



They were so reactive in polymerization that they were difficult to handle.

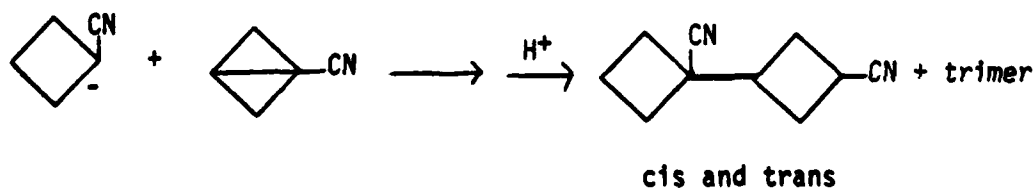
G. Electrophilic Bicyclobutane Monomers

1. Earlier Work

In the past, we investigated extensively bicyclobutanes with electronegative bridgehead substituents as new monomers. The most interesting polymer was poly-bicyclobutane-1-carbonitrile, . The long synthesis routes was the major obstacle for further development.

2. Recent Work

To elucidate the stereochemistry of the above bicyclobutane polymer, its CMR spectrum was analyzed by Professor M. Barfield of the University of Arizona. To assist his analysis, we prepared dimers and trimers with the above structures:



This should help to correlate stereostructure with physical polymer properties.

H. New Theories

We proposed three new theories:

1. A cation-radical propagation mechanism.
2. An anion-radical propagation mechanism.
3. An Organic Chemist's Periodic Table.

Personnel

(1977-1980)

J. H. Bentley - Graduate Student
D. Regelman - Post-doctoral
S. Snider - Graduate Student
J. Rhoades - Graduate Student
P. Nogues - Post-doctoral
G. Snow - Graduate Student
R. Cramer - Graduate Student

Cumulative List of Publications of H. K. Hall, Jr.'s
Research Group at the University of Arizona with
U. S. Army Support, 1971-present

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Cumulative List of Publications of H. K. Hall, Jr.'s
Research Group at the University of Arizona with
U.S. Army Support, 1971-present (Cont'd)

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H. K. Hall, Jr., J. E. Mulvaney and R. Cramer, "7,8-Dicyano-7,8-di-(methoxycarbonyl)quinodimethane," Polymer Bulletin, to be published.

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